



## Acceleration of a photochromic ring-opening reaction of diarylethene derivatives by excitation of localized surface plasmon

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### ABSTRACT

Localized-surface-plasmon (LSP)-enhancement effect on one-photon photochromic ring-opening reaction of two diarylethene (DE) derivatives was studied using absorption spectroscopy. DEs were doped in polymer films and those were coated onto Au-nanoparticles-integrated substrates. Acceleration of the one-photon photochromic reactions was observed in the presence of Au nanoparticles. The origin of the behavior was attributed to an enhancement effect of incident electromagnetic field by LSP. An alternative mechanism, i.e., photothermal effect was also experimentally examined and discussed.

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### 1. Introduction

Surface plasmon science, plasmonics, and their related applications have undergone explosive growth in the past decade [1,2], partly because of progresses in nanotechnologies. When a nanoparticle of a noble metal such as gold or silver is irradiated with resonant light, localized surface plasmon (LSP) would be excited and the electromagnetic field of incident light would be strongly localized around a metal surface, resulting in the enhancement of an electromagnetic field. A representative application of such LSP has been so-called SERS (Surface Enhanced Raman Scattering) that is observable from molecules adsorbed on a metal surface [3]. Fabrications of ultra-high-sensitive chemical sensors based on LSP have been an active area of research in analytical and medical sciences.

Beyond SERS application, nowadays LSP is being applied to photo-sciences such as photochemical reactions. Such applications of LSP toward photochemistry are called “plasmonic photochemistry” or “plasmon-enhanced photochemistry” [4]. Based on the enhancement effects, we may expect an increment of photochemical reaction yields in the presence of LSP. Several research groups have been reported such efficient LSP-enhancement for representative photochemical systems involving photocatalytic reaction [5], photoelectron-conversion [6], photobiological reactions [7], and so on. In addition to these normal photochemistry, LSP-enhanced elec-

tromagnetic field of light would frequently lead to a non-linear photo-process.

Indeed, Ueno and Misawa et al. first demonstrated that 2-photon absorption of a resin (SU-8) leading to photo-polymerization was achieved even by the irradiation of incoherent CW light [8]. They ascribed the origin of the 2-photon absorption to the enhancement of electromagnetic field by LSP. Furthermore, we also demonstrated such LSP-based 2-photon photochromic reaction, an important as well as a representative photochemical reaction [9]. Upon near infrared ( $\lambda = 808$  nm) CW light irradiation with moderate intensity (0.01–3.0 W/cm<sup>2</sup>), a diarylethene (DE) derivative underwent a ring-opening reaction, which was quantitatively monitored with absorption spectroscopy. The reaction yield was verified to be proportional to the square of light intensity, indicating the 2-photon reaction of DE. A considerably enhanced electromagnetic field of an incident light would result in the 2-photon absorption of these molecules located in the vicinity of metal nanoparticles.

Thus, LSP-enhanced photochemistry is of quite intriguing and valuable for challenging. Although various types of photochemical reaction should be explored in terms of LSP-enhancement, experimental examination has still been limited so far. It is noteworthy here that LSP interactions with DE derivatives have been investigated by Kobatake et al. in details: they reported that photochromic reactions can be detected with high sensitivity by monitoring LSP resonant wavelength for Au nanoparticles coated with a DE-linked polymer [10]. In the present study, we studied a LSP-enhancement effect on one-photon photochromic ring-opening reaction of DE derivatives. The photochromic ring-opening reaction (bleaching reaction) in DE is an important reaction in relation to applications of optical memory. However, quantum yield of ring-opening reac-

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tion is low generally and a method to improve it has been desired. We examined two types of LSP for DE: one is LSP at an individual Au nanoparticle [9], while the other one is LSP at “nano-gap” between adjacent Au nanoparticles (gap-mode LSP) [11,12]. The resonant optical wavelengths of the former and latter LSP locate around 500–600 nm and 600–1000 nm ( $\geq 600$  nm), respectively. Using the combination of both types of LSP, we can cover a wide wavelength region, resulting in a potential LSP application to the bleaching reaction of various colors of DE derivatives.

## 2. Materials and methods

Diarylethenes, 1,2-bis(2,4-dimethyl-5-phenyl-3-thienyl)-3,3,4,4,5,5-hexafluoro-1-cyclopentene (b-DE) and 1,2-bis(2-methyl-1-benzothiophen-3-yl)perfluorocyclopentene (r-DE) (Fig. 1), were used as received [13,14]. Two types of substrates on which gold nanoparticles were integrated were prepared by a similar manner to that reported previously. One is a glass substrate on which gold nanodimer arrays were integrated regularly was fabricated using a technique of angle-resolved nanosphere lithography (AR-NSL) whose details were described already [11,12]. The height of each dimer and the distance between adjacent dimers were evaluated to be 30 nm and 140 nm, respectively. The other one is a glass substrate that was introduced as the “substrate type I” in our previous work [9]. Gold nano-spheres (diameter = 30 nm) were chemically fixed onto a glass substrate. Surface structures and optical properties of these substrates are presented in the next section. Poly (methyl methacrylate) (PMMA) (Aldrich) doped with b-DE or r-DE was spin-coated onto a AR-NSL substrate or a substrate type I, respectively, using dichloroethane as a solvent. Doping concentration of DEs was 1–1.5 mol/l in PMMA films. Electronic absorption spectra were measured using a Hitachi U-3300 spectrometer. An atomic force microscope (AFM) was used in a tapping-mode (Seiko Instruments, SPI 3800). The film thickness was evaluated to be c.a. 10 nm by absorption spectroscopy and AFM. The film thickness was smaller than the height of gold nanoparticles in the two kinds of substrate, hence all of DE molecules should interact with surface plasmon of gold nanoparticles in the films.

Continuous wave (CW) lasers were used as excitation light sources:  $\lambda = 532$  nm (a DPSS laser), 633 nm (He–Ne laser), 670 nm (a laser diode), and 690 nm (laser diode). Irradiation power ( $P$ ) was kept below 1 mW/cm<sup>2</sup> at the sample surface. Irradiation experiments were carried out in a following manner. First, a film sample was irradiated with UV light for several tens of minutes to convert all DE molecules into its closed form in the film. This was used as a starting specimen. Next, the film was irradiated with visible laser light (633, 670, 690, and 532 nm) for a certain time to induce the photochromic ring-opening reaction, and an absorption spectrum of the film was measured to evaluate a reaction yield. Then, the film was irradiated with UV light again to recover it to the initial starting state. Then, again, the film was irradiated with the visible laser light, measured for absorption spectrum, and returned to the initial state by UV light irradiation. Such cyclic procedure was repetitively carried out to follow the ring-opening reaction. Each step of UV irradiation in the cyclic procedure was indispensable to guarantee the accuracy of experiments by the following reason. Accordingly with the film thickness, the absorbance of DE was quite low (see latter). Therefore, the absorbance was affected even by the absorption measurement itself (even monitoring light in the spectrometer also promoted the photochromic reaction). By analyzing temporal changes of absorption, we examine effect of surface plasmon on the photochromic reaction. For a temperature dependence experiment, a temperature controller (Tokai Hit, Thermoplate) used in irradiation.

## 3. Results and discussion

### 3.1. Characterization of samples

Fig. 2(a) and (b) shows absorption spectra of DEs. Also, absorption spectra of the two kinds of substrates are shown in the figure. The substrate showed two broad absorption bands. In the substrate type I (Fig. 2(a)), an absorption spectrum located around 550 nm is assigned to a well-known resonant surface plasmon band due to individual Au nano-particles as we reported already. In this case, each gold nanoparticle was isolated on a glass substrate and electronic interactions among nanoparticles should be weak or negligible. On the other hand, the AR-NSL substrate exhibited a broad band located in a longer wavelength side ( $>600$  nm) reaching to a near infrared region (Fig. 2(b)). The broad band should be ascribed to a “gap-mode absorption band” that originates from nano-gap in nano-blocks [11,12].

The absorption spectrum of r-DE in its closed form is largely overlapped with the resonant surface plasmon band of the substrate type I, while spectrum of b-DE is partly overlapped with the gap-mode band of the AR-NSL substrate. Namely, when we irradiate the former sample (r-DE/substrate type I) with a green light and irradiate the latter one (b-DE/AR-NSL substrate) with a red light, the lights excite both DEs (in its closed form) and surface plasmon. Thus, we can expect acceleration of a photochromic ring-opening photochemical reaction of DEs by excitation of LSP of Au nanoparticles.

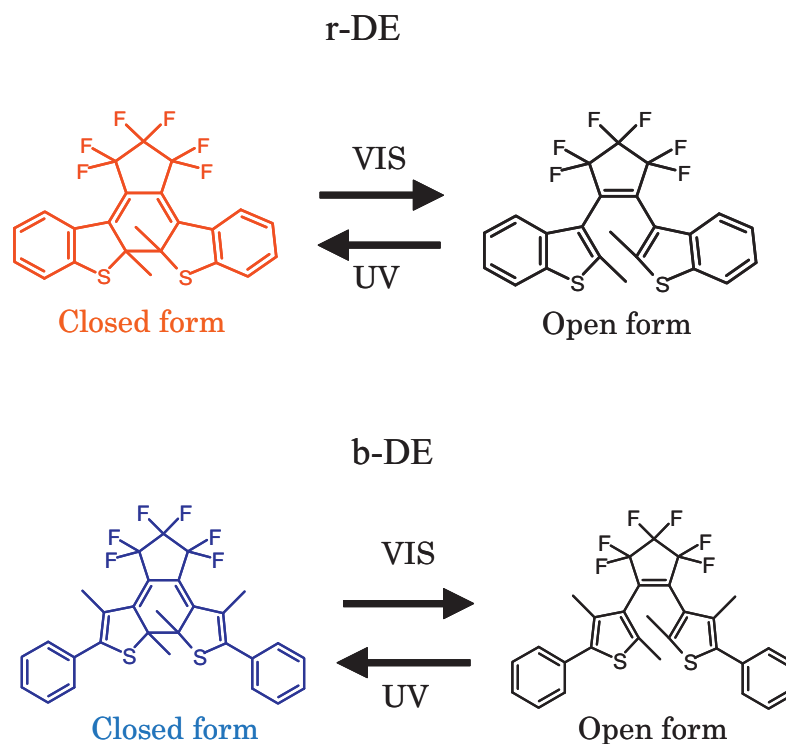
### 3.2. Irradiation experiments

We carried out irradiation experiments by a manner described above. Fig. 3 shows a result for the r-DE sample using the substrate type I irradiated with weak 532 nm laser light. The absorption spectra displayed in the figure were obtained by subtraction of the spectrum of the substrate itself from the spectrum of the sample (consisting of a film and a substrate). A film sample coated on a glass substrate was also examined as a reference without any plasmonic effect. In the reference spectrum (Fig. 3(a)), an absorption band of r-DE in its closed form was slightly decreased upon 532 nm irradiation, corresponding to a photochromic ring-opening reaction. Also the sample film on substrate type I exhibited decay of absorbance by irradiation (Fig. 3(b)). Here, we defined the extent of reaction as  $(A(0) - A(t))/A(0)$  where  $A(0)$  is an initial absorbance of DE and  $A(t)$  is the absorbance at a given time ( $t$ ). In Fig. 3(c), the extent of reaction was plotted against irradiation time. As seen, the decay rate in the sample film was obviously faster than that in the reference sample, implying an acceleration of the photochromic reaction due to an excitation of resonant LSP.

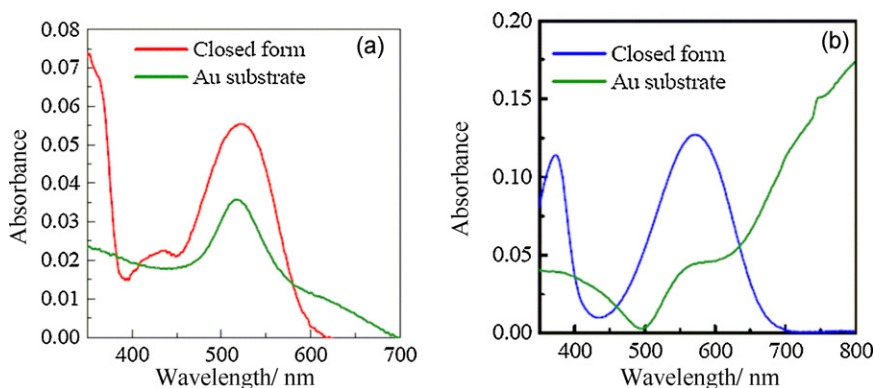
Such a plasmonic effect was observed also in b-DE by an excitation of a gap-mode. Also for b-DE films on NSL-substrates, we carried out irradiation experiments at 633, 670, and 690 nm. As a representative example, Fig. 4 shows results at 670 nm. As seen in the figures, an absorption band located at around 500–700 nm, which was safely ascribed to b-DE in its closed form, gradually decreased upon irradiation. The rate of ring opening reaction in the sample films on NSL-substrate was slightly faster than that in the reference sample, as the time dependences of reaction extent shown in the figure. This suggests an acceleration of the photochromic reaction due to an excitation of gap-mode surface plasmon.

### 3.3. Analysis of reaction efficiency

We can evaluate the reaction efficiency by analyzing above results on the basis of the following method. Time-dependent con-



**Fig. 1.** Molecular structures and photochromic reaction schemes of diarylethene (DE) derivatives used in the present study.



**Fig. 2.** Absorption spectra of (a) substrate type I and r-DE in its closed form and (b) AR-NSL substrate and b-DE in its closed form.

centration ( $C(t)$ ) of DEs in their closed form in a film should satisfy a differential equation noted below.

$$\frac{-dC(t)}{dt} = \frac{\Phi I_0 (1 - 10^{-A(t)})}{l} \quad (1)$$

where  $\Phi$  is a reaction quantum yield,  $I_0$  is an intensity of excitation light (number of photons ( $\text{mol}/\text{s cm}^{-2}$ )),  $A(t)$  is an absorbance maximum of a DE in a film sample as a function of time, and  $l$  is a path length (here we let  $l = 1$ ). Integration of Eq. (1) gave us an equation,

$$\ln(10^{A(t)} - 1) - \ln(10^{A(0)} - 1) = -2303\Phi\varepsilon I_0 t \quad (2)$$

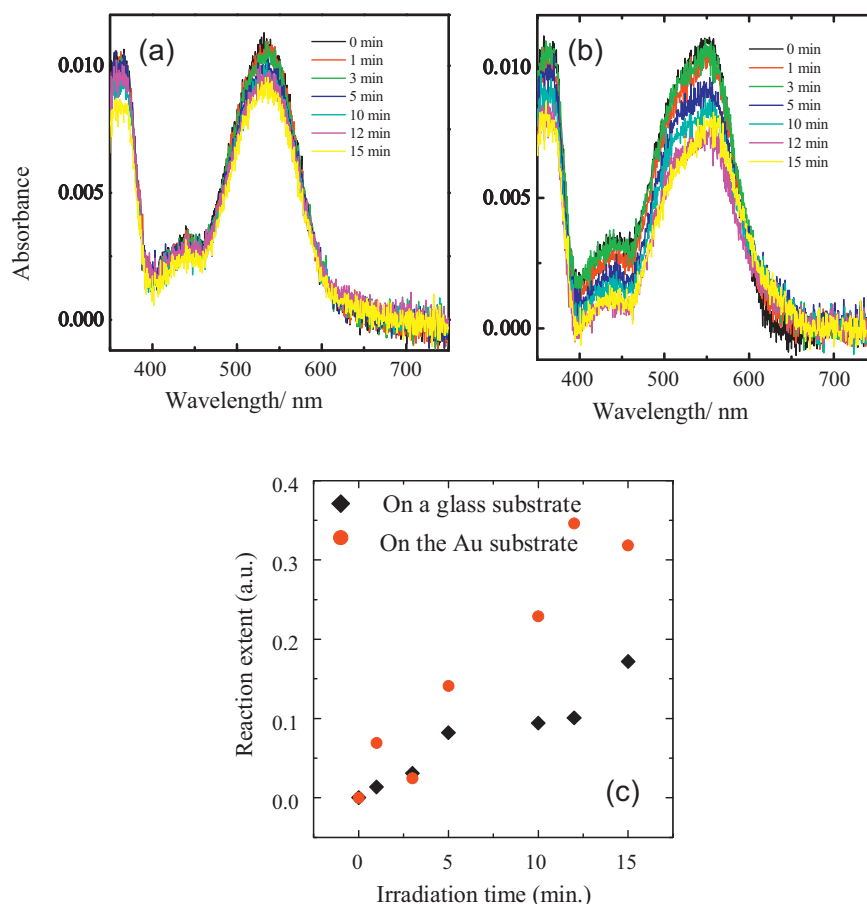
where  $A(0)$  is an initial absorbance of DE and  $\varepsilon$  [ $(\text{mol}/\text{l})^{-1} \text{cm}^{-1}$ ] is a molecular extinction coefficient of DE at the irradiation wavelength. When the left part of Eq. (2),  $\ln(10^{A(t)} - 1)$ , is plotted against the irradiation time ( $t$ ),  $\Phi$  is obtained in the slope of the plot. Such plots are shown in Fig. 5 where linear relations were roughly observed. Since the absorbance of samples films was very small ( $<0.02$ ), experimental error should not be negligible, resulting in the scattering of data points.

In Table 1, reaction quantum yields in the presence of gold ( $\Phi_{\text{Au}}$ ) and absence of gold ( $\Phi_{\text{glass}}$ ) are summarized for the three laser wavelength. The reaction quantum yield in the absence plasmon ( $\Phi_{\text{glass}}$ ) was evaluated to be 0.014–0.03 for b-DE, which was close to values previously reported by Irie's group within experimental error. Inspection of the table reveals here that the reaction yields  $\Phi$  are enhanced by the presence of plasmonic excitation for all the

**Table 1**  
Quantum yield of the ring-opening photochemical reactions in the present systems.

Compound	Irradiation wavelength (nm)	$\Phi_{\text{glass}}$	$A_{\text{Au}}$	$F(\Phi_{\text{Au}}/\Phi_{\text{glass}})$
r-DE	532	–	–	2.5 <sup>a</sup>
b-DE	633	0.027	0.04	1.5
b-DE	670	0.029	0.045	1.6
b-DE	690	0.014	0.021	1.5

<sup>a</sup> Absolute  $\Phi$  values were not determined and only the relative ratio ( $F$ ) was determined.



**Fig. 3.** Absorption spectral changes due to a ring-opening photochromic reaction of r-DE in a PMMA films on (a) a glass substrate and (b) a AR-NSL substrate. Irradiation wavelength and intensity were 532 nm and  $<1 \text{ mW/cm}^2$ , respectively. The extent of reaction  $((A(0) - A(t))/A(0))$ , see text) was plotted against the irradiation time in (c).

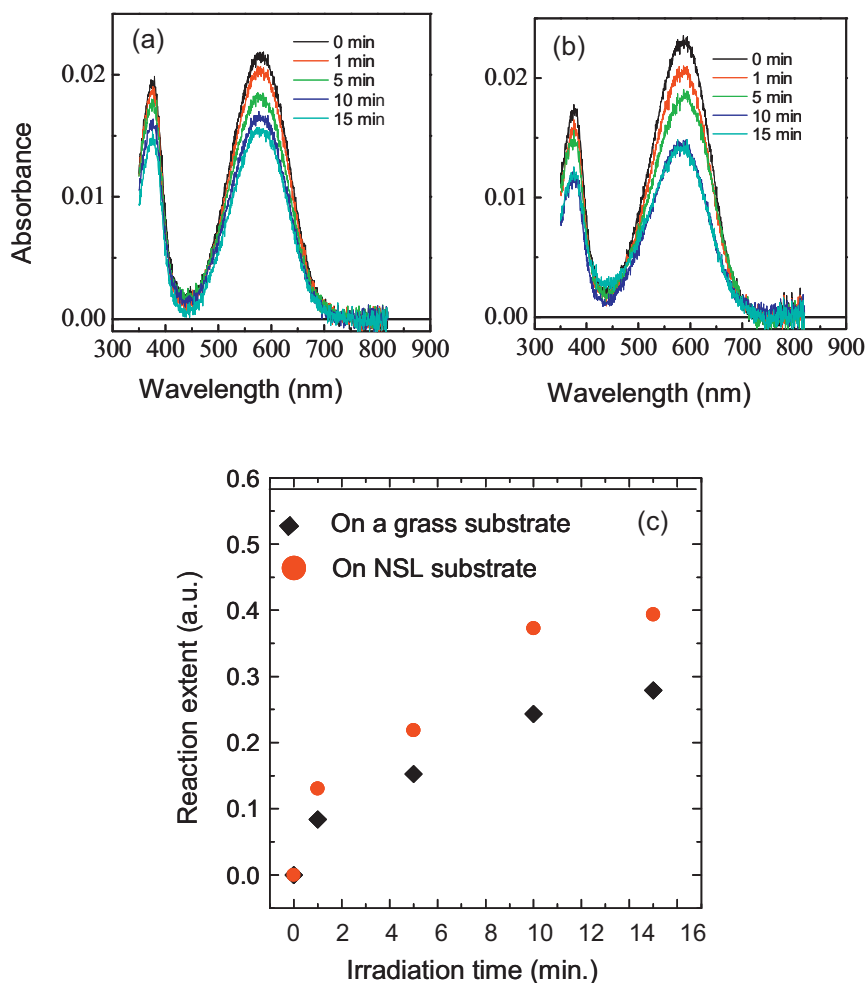
cases. The enhancement factor  $F$  ( $F = \Phi_{\text{Au}}/\Phi_{\text{glass}}$ ) was determined  $F=2.5$  for r-DE and  $F\sim 1.5$  for b-DE. It should be noted that the enhancement ( $F$ ) was commonly observed for b-DE irrespective to excitation intensity (see results at 690 nm excitation in the table). Also,  $F$  value for b-DE hardly depended on excitation wavelength (633, 670, 690 nm). These are natural since yields of linear (one-photon) photochemical reactions should not depend on the two excitation parameters.

#### 3.4. Mechanism of the reaction enhancement

In final, here we discuss a mechanism of the enhancement by the presence of LSP. Such enhancement effects in photochemical or photocatalytic reactions have frequently investigated by several groups. For instance, Chen et al. demonstrated that the photodecomposition of HCHO obviously was enhanced by the presence of gold nanoparticles [5]. El-Sayed's groups actively explored plasmonic photochemistry for various systems including biological systems [9]. Indeed, they revealed that excited state dynamics of bacteriorhodopsin is affected by the presence of gold nanoparticles. In such studies, to ascribe the enhancement of photochemical reactions to the LSP effect, an alternative effect, i.e., photothermal effects have been discussed and eliminated carefully. Indeed, it has frequently been reported that gold nanoparticles act as an efficient energy converter from light to heat upon resonant LSP excitation. Therefore, such a photothermal effect, a photochemical reaction is promoted by temperature elevation in the vicinity of gold nanoparticles, should be examined in the present case.

Unfortunately, little is known about temperature effect on yield of ring-opening reaction in DE derivatives. For instance, Cipoloni et al. reported it for DE derivatives having a Si atom or a PO ( $\equiv\text{P}=\text{O}$ ) group [15], whereas no report for the present system. Therefore, we investigated the temperature dependence of the reaction yield for the present system (b-DE). Quantum yield of the ring-opening reaction for a b-DE film on a glass substrate was measured at various temperatures. The yield at a given temperature ( $\Phi(T)$ ) was normalized with that at room temperature ( $\Phi_{RT}$ ), and plotted against temperature in Fig. 6. As seen in the figure,  $\Phi(T)$  hardly depended upon temperature; the ratio ( $\Phi(T)/\Phi_{RT}$ ) did not reach 2 even at  $90^\circ\text{C}$ . The enhancement factor  $F$  ( $F = \Phi_{\text{Au}}/\Phi_{\text{glass}}$ ),  $F=1.5\text{--}1.6$  (see Table 1) would correspond to  $T=60\text{--}70^\circ\text{C}$  in the photothermal model. However, such photothermal mechanism is obviously not for the present case, since the irradiation power used in the experiments of Figs. 3 and 4 was suppressed to be quite low ( $P < 1 \text{ mW/cm}^2$ ). For the present AR-NSL Au substrate, temperature elevation ( $\Delta T$ ) upon red light irradiation was estimated to be  $\Delta T < 0.001 \text{ K}$  when  $P \leq 1 \text{ mW/cm}^2$  [16]. Indeed, this  $P$  value was much lower than that used in past relevant studies;  $P=0.117 \text{ W/cm}^2$  for photo-oxidation of organic contaminants with gold nanoparticles [5], and  $P=0.5 \text{ W/cm}^2$  for proton-pump process of the bacteriorhodopsin in the presence of gold nano-rods [9]. Temperature rise ( $\Delta T$ ) was estimated to be  $100 \text{ K}$  and  $10^{-2} \text{ K}$  in the former and latter studies, respectively. Namely, any photothermal effect is completely negligible in the present case using  $P=1 \text{ mW/cm}^2$ .

Thus, based on the above discussion, we ascribe the origin of the reaction acceleration to the plasmon field enhancement. This mechanism is interpretable as the following manner [4]. In the

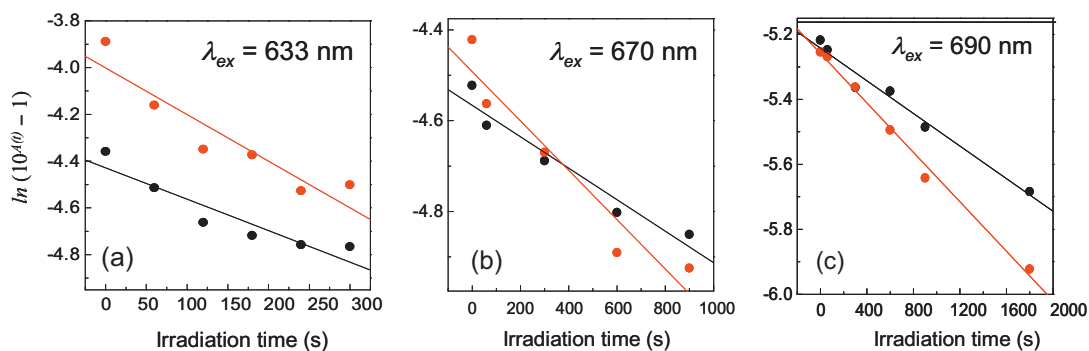


**Fig. 4.** Absorption spectral changes due to a ring-opening photochromic reaction of b-DE in a PMMA films on (a) a glass substrate and (b) a AR-NSL substrate. Irradiation wavelength and intensity were 670 nm and 0.9 mW/cm<sup>2</sup>, respectively. The extent of reaction  $((A(0) - A(t))/A(0))$ , see text) was plotted against the irradiation time in (c).

present case, incident light wavelength was tuned to the surface plasmon resonance, LSP of an isolated gold nano particle at 532 nm or gap-mode LSP of a gold dimer at 633–690 nm. In such resonant irradiation condition, the electric field  $E_p$  in the vicinity of gold surface is expressed as  $E_p = gE_0$ , where  $E_0$  is the electric field of an incident light and  $g$  is an enhancement factor ( $g = 10\text{--}10^{2.5}$ , generally). On the hand, the interaction between a molecule and the enhanced electric field would depend upon a term of  $-\mu E_p$  in a matrix element of interaction energy, where  $\mu$  is the dynamic molecular dipole. In analogy to a one-photon allowed molecu-

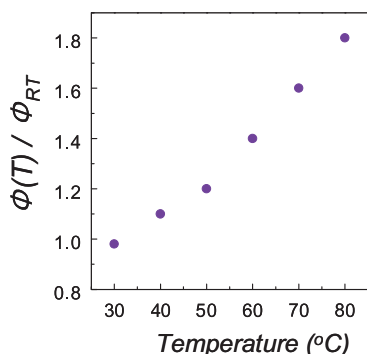
lar transition (i.e., optical absorption), the probability of optical absorption of the molecule is proportional to the square of this term ( $-\mu E_p$ ) based on the Fermi's golden rule, resulting in an "enhanced molecular absorption". In accordance with this process, a yield of photochemical reaction following light absorption would be increased by LSP.

Here, one question will rise in the framework of above model. The plasmon enhancement of a photochemical reaction should show a factor of  $10^2\text{--}10^5$  since it is proportional to  $g^2$ . On the other hand, the enhancement factor was observed to be 1.3–2.5



**Fig. 5.** Photochemical analysis to give reaction quantum yields  $\Phi$ ;  $\ln(10^{A(t)} - 1)$ , is plotted against the irradiation time ( $t$ ) and  $\Phi$  is obtained in the slope of the plot. The lines in the figure are best fit to experimental data points with a least square method. Irradiation wavelength is noted in the figure.





**Fig. 6.** Temperature dependence of a ring-opening reaction in b-DE. Quantum yield ( $\Phi(T)$ ) at a given temperature was normalized with the room temperature ( $\Phi_{RT}$ ). Irradiation wavelength was 532 nm ( $P < 1 \text{ mW/cm}^2$ ).

at most, which was much lower than the value predicted. It should be noted that such small enhancement factor ( $<10$ ) has frequently been reported in past relevant studies. For instance, Awazu et al. reported that a  $\text{TiO}_2$ -catalyzed photodecomposition of a dye molecule (methylene blue) was enhanced by a factor of 7 in the presence of silver nanoparticles. In a large part of past studies on plasmon-enhanced fluorescence, the enhancement factors barely reached to 10 at most. El-Sayed's group reported that relaxation rates of excited intermediate states in a photosynthesis system (bacteriorhodopsin) were made to be fast or slow by a factor of 1.5 in the presence of gold nanoparticles.

A tentative explanation for the small enhancement value in the present study is as follows. In our sample films, DE molecules should be dispersed with a broad distribution with respect to the distance ( $d$ ) between DE molecules and gold nanoparticles. DE molecules that is far from gold nanoparticles or nano-dimmers ( $d > \text{few tens of nm or } 10 \text{ nm}$ ) would be hardly affected by plasmonic field, and their reaction yield would not be increased accordingly. By contrast, DE molecules that are located in the vicinity of gold nano particles ( $d < 10 \text{ nm}$ ) can interact with plasmonic field efficiently, resulting in the enhancement of the reaction. On the other hand, when DE molecules move closer to gold nanoparticles ( $d < 5 \text{ nm}$ ), quenching of the excited DE state by gold nanoparticles (electronic energy from DE to gold) would be dominant rather than plasmonic enhancement, leading to damping of the reaction. Although these 3 types co-exist in sample films, we observed all of them and determined the enhancement factors in average. If we evaluate the reaction efficiency for these 3 types separately, we presumably observe more distinct enhancement for DE molecules by LSP.

## 4. Conclusion

Photo-excitation of localized surface plasmon both in an isolated surface resonant mode ( $\lambda_{\text{ex}} = 532 \text{ nm}$ ) and a gap mode ( $\lambda_{\text{ex}} = 633, 670, 690 \text{ nm}$ ) can promote the photochromic ring opening reactions. Since any photothermal effects are completely negligible, the origin of the observed behavior is ascribable to the effects of plasmonic field (enhanced electromagnetic field of incident light). The enhancement factor was obtained to be small value, 1.5–2.5. However, this value can be improved by optimization of plasmonic substrates (increasing nano-gap density or narrowing down the gap width, etc.) potentially.

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